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## GAS CHROMATOGRAPHIC STUDIES ON GROUP VIB ORGANOMETALLIC COMPLEXES

### THE ANALYTICAL AND PREPARATIVE SEPARATION OF CHROMIUM, MOLYBDENUM AND TUNGSTEN TRIFLUOROPHOSPHINE CARBONYL COMPLEXES

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#### SUMMARY

The separation and determination of isomeric trifluorophosphine carbonyl complexes of chromium, molybdenum, and tungsten have been achieved. Both analytical and preparative separations have been carried out on the synthetic products obtained from the irradiation of the metal hexacarbonyl in the presence of trifluorophosphine. Product composition was confirmed by infrared spectrophotometry. Chromatographic figures of merit were calculated to indicate column performance for these compounds.

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#### INTRODUCTION

Gas chromatography has been extensively applied to the analysis of organometallic compounds<sup>1</sup>. However the majority of work on the Group VIB metals has been limited to the separation of arene chromium tricarbonyls. Veening and co-workers<sup>2-4</sup> have separated benzene, toluene, mesitylene, durene, hexamethylbenzene and fluorobenzene tricarbonyl chromium compounds. They have also separated the ring isomeric methylbenzene tricarbonyl chromium complexes<sup>5</sup> using either a packed glass column with 3.6% SE-30 or a support-coated open tubular column packed with *m*-bis(*m*-phenoxy)benzene and Apiezon-L. The *cis-trans* isomer ratios of alkylindane tricarbonyl chromium complexes were determined by Jackson and co-workers<sup>6,7</sup> as well as the isomeric distributions of the alkylbenzene tricarbonyl chromium complexes following Friedel-Crafts acetylation<sup>8</sup>. The chromatography of substituted thiophene tricarbonyl chromium complexes has been carried out by Segard *et al.*<sup>9</sup> The literature on molybdenum and tungsten carbonyl separations is limited to two works. Pommier and Guiochon<sup>10</sup> separated iron pentacarbonyl from chromium, molybdenum, and tungsten hexacarbonyl and Clark and Hobermann<sup>11</sup> reported the relative retention times for molybdenum trifluorophosphine carbonyls.

In this report, we present the first systematic investigation of the separation of

Group VIB metal carbonyls substituted with trifluorophosphine ( $\text{PF}_3$ ). These compounds are octahedral complexes substituted with  $\text{PF}_3$ . The metal complexes substituted with two and four  $\text{PF}_3$  groups give rise to *cis* and *trans* geometrical isomers while the triply substituted species yields *facial* and *meridial* geometrical isomers. The ability to quantify and identify the individual components  $\text{M}(\text{PF}_3)_x(\text{CO})_{6-x}$  ( $\text{M} = \text{Cr, Mo, or W; } x = 0-4$ ) in a mixture obtained in the synthetic reactions with various metals was needed. Infrared spectroscopy is not fully suitable for quantitation and identification of these complexes due to extensive band overlap. Work is continuing on the determination of thermodynamic equilibrium constants for the various systems as equilibrium is approached either thermally or photochemically. Both the  $x$  values and isomeric ratios are needed. The molybdenum carbonyl trifluorophosphine complexes have been used to study the hot-atom chemistry of molybdenum and technetium<sup>12</sup>. The tungsten analogs have been recently synthesized and are being used to study the chemical behavior of the tungsten complexes following thermal neutron capture. Well resolved chromatograms are necessary to track the generation of new species in the hot-atom process<sup>13</sup>.

## EXPERIMENTAL

### Reagents

Chromium and tungsten hexacarbonyls were purchased from Strem Chemical, and molybdenum hexacarbonyl was purchased from Pressure Chemical. All were used without further purification.  $\text{PF}_3$  was synthesized from antimony trifluoride and phosphorous trichloride in acetonitrile with antimony pentachloride as a catalyst. The  $\text{PF}_3$  gas was trapped at  $-196^\circ\text{C}$  and it was purified by bubbling it through a 24-in. water tower. Water was removed by vacuum distillation from a  $-128^\circ\text{C}$  methylcyclohexane bath. The  $\text{PF}_3$  was checked by infrared spectroscopy for purity. Perfluorohexane from PCR Research Chemicals was the solvent used in the separation.

### Synthesis

An amount of 10 g of metal carbonyl was placed in a pyrex flask equipped with a Kovar seal and a metal valve. It was thoroughly degassed and  $\text{PF}_3$  was admitted to a pressure of approximately one atmosphere. The flask was then irradiated at  $70^\circ\text{C}$  for 4-12 h with a water cooled 450-W Hanovia UV source. The evolved carbon monoxide was pumped off at  $-196^\circ\text{C}$  and replaced with  $\text{PF}_3$ . The irradiation/pump cycle was repeated until no crystalline  $\text{M}(\text{CO})_6$  was visible. The resulting liquid consisted of  $\text{M}(\text{PF}_3)_x(\text{CO})_{6-x}$  ( $\text{M} = \text{Cr, Mo, or W; } x = 0-4$ ). These compounds will be abbreviated as follows:  $\text{M}(\text{PF}_3)(\text{CO})_5 = \text{MP}_1\text{C}_5$ ;  $\text{M}(\text{PF}_3)_2(\text{CO})_4 = \text{MP}_2\text{C}_4$ ;  $\text{M}(\text{PF}_3)_3(\text{CO})_3 = \text{MP}_3\text{C}_3$ ;  $\text{M}(\text{CO})_6 = \text{MC}_6$ .

### Apparatus and equipment

An Aerograph Autoprep A-700 gas chromatograph was used equipped with a thermal conductivity detector and an automatic collector. A Houston Instrument Recordall Series 500 integrating recorder was used at 1 mV input. The column for analytical work was a 12 m  $\times$  1/4 in. copper tube packed with Chromosorb P (30-60 mesh) coated with 35% DC 702 silicone oil. The preparative column was a 12 ft.  $\times$  3/8 in. copper tube packed with 40% DC 703 silicone oil on Chromosorb P

(30–60 mesh). The carrier gas was hydrogen. A Perkin-Elmer 983 infrared spectrophotometer was used for the infrared identification. The invariant instrumental conditions for the analytical work were the following: detector temperature, 100°C; injector temperature, 115°C; detector current, 140 mA.

### Procedure

For the analytical separation, the viscous synthetic mixture was diluted with an equal volume of perfluorohexane. Injections (2  $\mu$ l) were made in triplicate with a 10- $\mu$ l Hamilton syringe to ascertain retention times using the air peak as time zero. Each peak was trapped at  $-30^\circ\text{C}$ . Each component was then dissolved in spectrograde hexane and an infrared spectrum was obtained in the range 1800–2200  $\text{cm}^{-1}$ . The preparative scale separations involved double separations. A volume of 125  $\mu$ l of a mixture  $[\text{M}(\text{PF}_3)_x(\text{CO})_{6-x}, x = 1-4]$  was injected at  $110^\circ\text{C}$  and fractions collected at  $-30^\circ\text{C}$ . Under these conditions the isomers were not separated. The isomeric fractions *cis*- and *trans*- $\text{M}(\text{PF}_3)_2(\text{CO})_4$  and *facial*- and *meridial*- $\text{M}(\text{PF}_3)_3(\text{CO})_3$  were then separated on the analytical column. The volume of either the di- or trisubstituted metal carbonyls was increased until the separation degraded beyond usefulness, usually 50–80  $\mu$ l per injection. These compounds are toxic and hence all chromatographic studies were carried out in fume hoods.

### RESULTS AND DISCUSSION

It has been determined that  $\text{M}(\text{PF}_3)_x(\text{CO})_{6-x}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{or W}; x = 1-4$ ) can be separated both preparatively and analytically. The preparative separation varied from the analytical separation only in peak shape and resolution. In preparative work, the peaks are broader and decidedly asymmetric. Often one isomer shows up as a shoulder on the other isomer rather than as two resolved peaks. The analytical separation of  $\text{M}(\text{PF}_3)_x(\text{CO})_{6-x}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{or W}; x = 0-4$ ) is shown in Figs. 1–3. The elution pattern is consistent between metals with the most highly substituted metal carbonyl eluting first ( $\text{MP}_4\text{C}_2$ ) and the hexacarbonyl eluting last. The hexa-

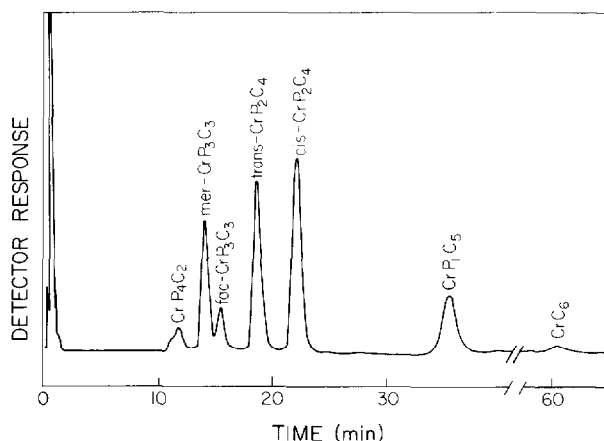


Fig. 1. Gas chromatographic separation of  $\text{Cr}(\text{PF}_3)_x(\text{CO})_{6-x}, x = 0-4$ . Column temperature:  $70^\circ\text{C}$ . Carrier gas: hydrogen (40 ml/min).

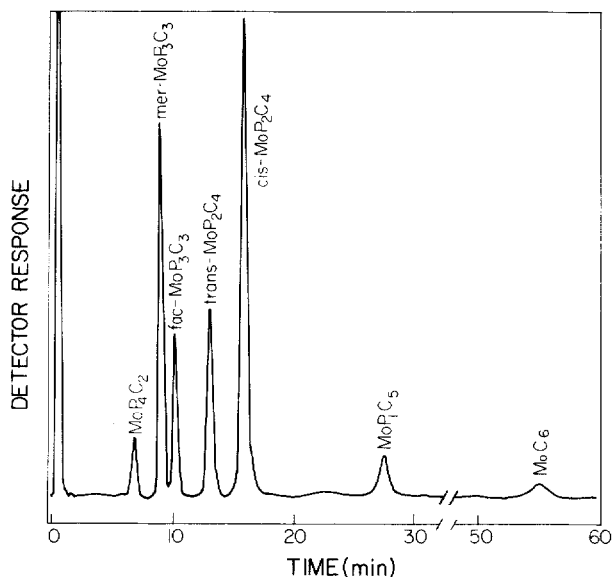


Fig. 2. Gas chromatographic separation of  $\text{Mo}(\text{PF}_3)_x(\text{CO})_{6-x}$ ,  $x = 0-4$ . Column temperature:  $100^\circ\text{C}$ . Carrier gas: hydrogen (56 ml/min).

carbonyl was added to saturation to the synthetic mixtures as a marker, however its retention time was too long to be useful with these columns. Temperature programming would bring the monosubstituted carbonyl and the hexacarbonyl into a more useful analytical range. The *facial* and *meridial*  $\text{MP}_3\text{C}_3$  isomers are barely resolved by GLC while *cis*- and *trans*- $\text{MP}_2\text{C}_4$  are cleanly resolved. The *cis* and *trans*  $\text{MP}_4\text{C}_2$  isomers are not resolved on this column but clear evidence of two components can be seen in Fig. 1 for chromium. The most symmetrical of any two isomer pairs always eluted first.

Even though the retention of the hexacarbonyl peak was overly long, these times illustrate the increased volatility of these compounds. In this study there is a monotonic relationship between volatility and the retention time. The vapor pres-

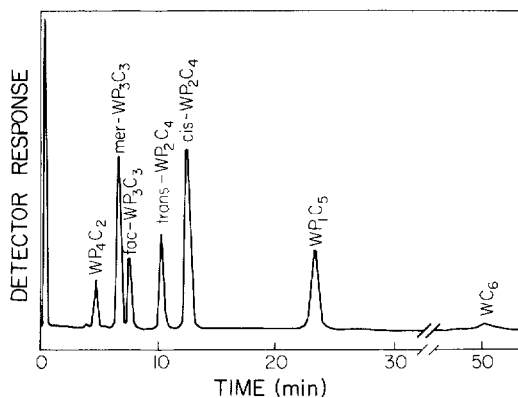


Fig. 3. Gas chromatographic separation of  $\text{W}(\text{PF}_3)_x(\text{CO})_{6-x}$ ,  $x = 0-4$ . Column temperature:  $100^\circ\text{C}$ . Carrier gas: hydrogen (85 ml/min).

TABLE I

CARBONYL STRETCHING FREQUENCIES ( $\text{cm}^{-1}$ ) FOR  $\text{M}(\text{PF}_3)_x(\text{CO})_{6-x}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ,  $x = 1-4$ )<sup>\*</sup>

Relative peak intensity: s = strong; ms = moderately strong; m = moderate.

Compound	Metal		
	Cr	Mo	W
MP <sub>4</sub> C <sub>2</sub>	2033.5 (s)	2046.9	2042.1
	1996.4 (s)	2010.4	2002.9
	1976.8 (m)	1989.6	1982.6
Meridial-MP <sub>3</sub> C <sub>3</sub>	2059.6 (m)	2068.8	2065.4
	2002.9 (s)	2014.0	2005.9
	1980.5 (s)	1988.0	1983.7
Facial-MP <sub>3</sub> C <sub>3</sub>	2053.8 (s)	2063.2	2059.7
	2000.8 (s)	2011.4	2003.9
Trans-MP <sub>2</sub> C <sub>4</sub>	1983.1 (s)	1989.2	1983.7
Cis-MP <sub>2</sub> C <sub>4</sub>	2076.5 (m)	2083.3	2081.8
	2004.2 (ms)**	2011.5**	2003.9**
	1982.6 (s)	1989.7	1938.7
MP <sub>1</sub> C <sub>5</sub>	2095.5 (m)	2100.6	2100.6
	2009.0 (s)	2013.0	2005.4
	1985.8 (s)	1988.2	1983.7

<sup>\*</sup> Uncertainty is  $\pm 0.2 \text{ cm}^{-1}$ .<sup>\*\*</sup> Two overlapping bands.

tures are known approximately by distillation experiments and increase as the PF<sub>3</sub> substitution increases up to  $x = 4$ . A plot of  $\log t'_R$  versus number of PF<sub>3</sub> groups was not linear but decreased in a curvilinear fashion. The observed relationship between retention time and PF<sub>3</sub> substitution also holds for nickel trifluorophosphine carbonyl complexes. However, for the nickel system the volatility decreases as the PF<sub>3</sub> substitution increases<sup>14</sup>.

The infrared spectra of all the components are shown in Table I for the 1800–2200  $\text{cm}^{-1}$  carbonyl region. The compounds are positively identified by comparing their spectra with those of the molybdenum compounds. The molybdenum species have been identified by a number of techniques including theoretical calculation of the peak positions and intensity by a factored force field method by Haas and Sheline<sup>15</sup>. Group theoretical considerations predict two carbonyl stretches for the *cis*-tetraphosphine and one for the *trans*-isomer. The unresolved first elution peak (MP<sub>4</sub>C<sub>2</sub>) shows the three carbonyl stretches expected for a composite of the *cis*- and *trans*-isomers. The rest of the data is in excellent agreement with the derived data. This is the first time that the spectra of the chromium and tungsten compounds have been published. The molybdenum species are included to show the data obtained on a single instrument so that a consistent set of values will be presented.

Some chromatographic parameters are tabulated in Tables II–IV for chromium, molybdenum and tungsten, respectively.  $K'$  was calculated as  $t'_R/t_m$  where  $t_m$  was the time for air passage. The capacity factor  $k'$  varies from 2.6 to 24.2 with only MP<sub>1</sub>C<sub>5</sub> and MC<sub>6</sub> outside the useful analytical range of  $1 < k < 8$ . This could be remedied by temperature programming. The symmetry factor is given by the back

TABLE II  
CHROMATOGRAPHIC PARAMETERS FOR  $\text{Cr}(\text{PF}_3)_x(\text{CO})_{6-x}$ ,  $x = 0-4$

Chromatographic conditions as in Fig. 1.

Compound	$t'_R$ (min)	$k'$	$N_{eff}$	Symmetry factor
$\text{CrP}_4\text{C}_2$	$11.9 \pm 0.2$	3.5		
Meridial- $\text{CrP}_3\text{C}_3$	$14.1 \pm 0.3$	4.0	1721	106
Facial- $\text{CrP}_3\text{C}_3$	$15.5 \pm 0.2$	4.4	2080	121
Trans- $\text{CrP}_2\text{C}_4$	$18.7 \pm 0.4$	5.3	2619	140
Cis- $\text{CrP}_2\text{C}_4$	$22.3 \pm 0.5$	6.4	2755	107
$\text{CrP}_1\text{C}_5$	$35.3 \pm 0.5$	10.1	3522	76
$\text{CrC}_6$	$60.4 \pm 0.5$	17.2	4028	132

TABLE III  
CHROMATOGRAPHIC PARAMETERS FOR  $\text{Mo}(\text{PF}_3)_x(\text{CO})_{6-x}$ ,  $x = 0-4$

Chromatographic conditions as in Fig. 2.

Compound	$t'_R$ (min)	$k'$	$N_{eff}$	Symmetry factor
$\text{MoP}_4\text{C}_2$	$6.8 \pm 0.1$	2.6		
Meridial- $\text{MoP}_3\text{C}_3$	$9.1 \pm 0.2$	3.4	1463	91
Facial- $\text{MoP}_3\text{C}_3$	$10.4 \pm 0.2$	4.0	1911	71
Trans- $\text{MoP}_2\text{C}_4$	$13.3 \pm 0.3$	5.1	2722	83
Cis- $\text{MoP}_2\text{C}_4$	$16.0 \pm 0.2$	6.1	2216	86
$\text{MoP}_1\text{C}_5$	$27.6 \pm 0.1$	10.5	4220	100
$\text{MoC}_6$	$55.0 \pm 0.3$	20.9	5410	103

half width ( $b$ ) divided by the front half ( $a$ ) at 10% peak height times 100. This is a figure of merit for the asymmetry of the peak due to overloading and injection problems. The symmetry factors varied from 71 to 132. This variation was mostly due to errors in the manual calculation of the symmetry. It is clear that even with these long retention times the peaks are not too distorted. The effective number of theoretical plates,  $N_{eff}$  was calculated by  $N_{eff} = 5.54 (t'_R/W_{1/2})^2$  where  $W_{1/2}$  is the full width at half height. The effective number of plates increased as the capacity factor increased.

TABLE IV  
CHROMATOGRAPHIC PARAMETERS FOR  $\text{W}(\text{PF}_3)_x(\text{CO})_{6-x}$ ,  $x = 0-4$

Chromatographic conditions as in Fig. 3.

Compound	$t'_R$ (min)	$k'$	$N_{eff}$	Symmetry factor
$\text{WP}_4\text{C}_2$	$4.9 \pm 0.1$	2.6	831	
Meridial- $\text{WP}_3\text{C}_3$	$6.8 \pm 0.2$	3.2	1323	105
Facial- $\text{WP}_3\text{C}_3$	$7.7 \pm 0.2$	3.7	1697	90
Trans- $\text{WP}_2\text{C}_4$	$10.5 \pm 0.1$	5.0	2259	80
Cis- $\text{WP}_2\text{C}_4$	$12.8 \pm 0.3$	6.1	2521	101
$\text{WP}_1\text{C}_5$	$23.6 \pm 0.2$	11.3	4821	94
$\text{WC}_6$	$50.6 \pm 0.3$	24.2	3546	

This is a function of the phase ratio  $\beta$ . The phase ratio  $\beta$  is defined as  $V_m/V_l$  where  $V_m$  is the gas volume and  $V_l$  is the volume of liquid phase. For heavy liquid loadings,  $\beta$  is small and  $N_{\text{eff}}$  increases with  $k'$  for low- $\beta$  columns such as the type used. Resolution is dependent on  $\beta$  and increases as  $\beta$  decreases. At lower liquid loadings the resolution was not sufficient to separate the isomeric species. The loadings and length was increased until resolution of the  $\text{MP}_3\text{C}_3$ 's was achieved.

The phase ratio is not the only phenomenon which influences retention of these fluorinated compounds. The column support at low liquid loadings can contribute to the retention behavior through adsorption activity. Veening and Huber<sup>16</sup> describe the relative contribution of adsorption onto the solid support *versus* solution into the stationary phase for chromium(III) and ruthenium(III) tris(trifluoroacetylacetonato) complexes as a function of liquid loading. At the higher loadings many of the active sites are "coated". Even so, for our compounds all new columns do not allow compounds to be eluted until 20–50  $\mu\text{l}$  have been injected. Upon deactivation of these sites on the solid support the columns functioned as illustrated in Figs. 1–3. These compounds are somewhat air and moisture sensitive and are not stable on some of the stationary phases that were tried. No decomposition was found on the columns used in this study. Radioactive  $\text{W}(\text{PF}_3)_x(\text{CO})_{6-x}$ ,  $x = 0-4$ , was separated on the analytical column and counted on a Na(I) well. Collection efficiencies were always 95–105% indicating no decomposition on column. The uncertainty in the percentages were due to counting statistics and counting geometry.

To show relative retention times, all the complexes  $\text{M}(\text{PF}_3)_x(\text{CO})_{6-x}$  ( $\text{M} = \text{Cr, Mo, or W}$ ;  $x = 0-4$ ) were chromatographed under the same conditions. These conditions were: column temperature, 100°C; detector temperature, 100°C; injector temperature, 115°C; and carrier gas, hydrogen, at a flow-rate of 67 ml/min. The column was 15 m packed with 40% DC-702 on Chromosorb P (30–60 mesh). The adjusted retention times were plotted as a function of atomic weight of each metal

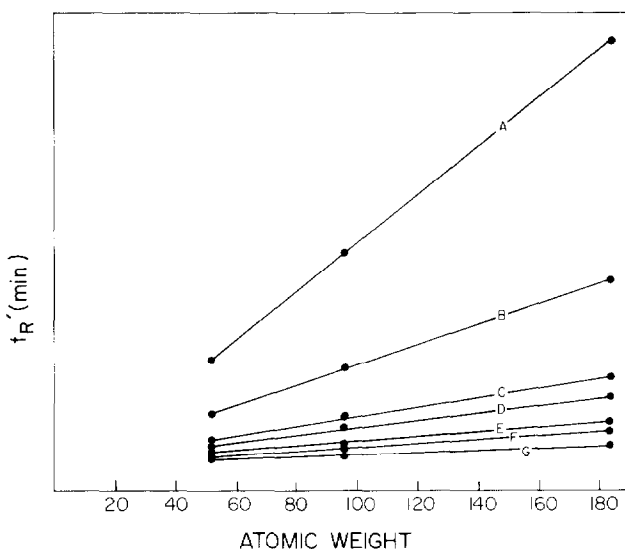


Fig. 4. Adjusted retention time *versus* atomic weight of metal (Cr, Mo, or W). A =  $\text{MC}_6$ ; B =  $\text{MP}_1\text{C}_5$ ; C = *cis*- $\text{MP}_2\text{C}_4$ ; D = *trans*- $\text{MP}_2\text{C}_4$ ; E = *mer*- $\text{MP}_3\text{C}_3$ ; F = *fac*- $\text{MP}_3\text{C}_3$ ; G =  $\text{MP}_4\text{C}_2$ .

in Fig. 4. The ability to separate a complex of any given composition of one metal from another decreases as the  $\text{PF}_3$  substitution increases. This type of plot will enable predictions to be made for separation of any group of metal trifluorophosphines.

The separation of Group VIB metal carbonyls substituted with trifluorophosphine has been found to be reliable and accurate. The *cis*- and *trans*-isomers of  $\text{M}(\text{PF}_3)_2(\text{CO})_4$  have also been separated both analytically and preparatively. A systematic investigation of the thermal stability of these compounds has not been conducted. However, thermal decomposition yielding gaseous reaction products decreases in the order molybdenum > chromium > tungsten. The stability of the species for a given metal increases as the  $\text{PF}_3$  content increases. *Cis-trans* isomerization for  $\text{MP}_2\text{C}_4$  has been observed at high temperatures, however the conditions reported in this paper avoid all the above reactions. Gas chromatography is currently the only technique with adequate resolving power to separate these complexes. Their sensitivity to protic solvents eliminates many other techniques. Separation by spinning band distillation techniques on a 24 in. column were not successful because the boiling points of all the compounds were too close to one another. These well resolved chromatograms have enabled the preparation of pure compounds for hot-atom irradiation studies as well as the post irradiation analysis. Because the isomers can be separated, the hot-atom process can be tracked for isomerization and generation of new chemical species. Future studies on the hot-atom process in the gas phase will be carried out for the tungsten compounds. The kinetic isomerization of *cis*- and *trans*- $\text{M}(\text{PF}_3)_2(\text{CO})_4$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ) will also be monitored by gas chromatography.

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